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In figures 2 and 3 the crosses indicate the position of stars of the sub-types B0, B1, and B2, and the dots refer to the sub-types B3 and B5. Stars of the first group of sub-types are believed to be intrinsically brighter than those of the second. For a given apparent magnitude, therefore, their distances are greater—possibly even twice as great. It is to be noted that the crosses have completely left the secondary circle in figure 3, indicating that the local cluster is not large enough to include objects as distant as B1 stars must be when they appear fainter than magnitude 7.

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[1] Shapley, Harlow, these PROCEEDINGS, 4, 1918, (224–229); *Mt. Wilson Communications*, No. 54. See also *Mt. Wilson Contr.*, No. 157, and a small modification of the original statement of a star-streaming hypothesis, *Mt. Wilson Contr.*, No. 161, section IX.

[2] For other properties of the local cluster and for a discussion of the peculiar value of B-type stars in describing its extent, form, and orientation, reference may be made to *Mt. Wilson Contr.*, No. 157, part II. and No. 161, section IX.

[3] Strömberg, Gustaf, *Astrophys. J., Chicago, Ill.*, 47, 1918, (7–37); *Mt. Wilson Contr.*, No. 144.

INFLUENCE OF IONS ON THE ELECTRIFICATION AND RATE OF DIFFUSION OF WATER THROUGH MEMBRANES

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1. When pure water is separated from a watery solution by a strictly semipermeable membrane more molecules of water will diffuse through the membrane from the pure solvent to the solution than will diffuse simultaneously in the opposite direction; and this difference in the rate of diffusion of water in the two opposite directions will be the greater the higher the concentration of the solution. When the solution is put under pressure, the number of molecules of water diffusing in the unit of time from the solution into the pure solvent will be increased and if this pressure reaches a certain value the number of molecules of water diffusing simultaneously in opposite directions through the membrane will become equal. We may therefore define the osmotic pressure of the solution as the additional pressure which has to be applied to the solution in order to cause as many molecules of water to diffuse from the solution to the pure solvent as will diffuse simultaneously in the opposite direction.

van't Hoff's theory of osmotic pressure assumes that this quantity depends exclusively upon the concentration of the solution. For some time it had been known that in certain cases water is able to diffuse from solutions of higher to solutions of lower concentrations, and it has been suggested by a number of authors, e.g., Girard,[1] Bartell,[2] Bernstein,[3] and others that these phenomena are due to electrical forces caused by the presence of electrolytes in solution. They assume on the basis of the experimental and theoretical work done by Quincke, Helmholtz, Perrin,[4] and others on electrical endosmose that differences of electrical potential on both sides of the membrane influence the rate of diffusion of water through the membrane.

The writer has recently investigated the influence of electrolytes on the rate of diffusion of water through collodion bags prepared in a definite and uniform way and bathed over night in a 1 per cent gelatin solution. The bags had the shape of Erlenmeyer flasks with 50 cc. contents and were closed by rubber stoppers which were perforated by a glass tube with a bore of 2 mm., the tube serving as a manometer.

When such a bag was filled with watery solution and was dipped into distilled water the level of the water in the manometer rose owing to the fact that more water diffused from the pure water into the solution than diffused simultaneously in the opposite direction, as was to be expected. It was found that the initial rate of diffusion of water was influenced in an entirely different way by electrolytes and non-electrolytes. The solutions of non-electrolytes, e.g., sugars, influenced the initial rate of diffusion of water through the membrane in proportion to their concentration and this influence began to show itself when the concentration of the sugar was above M/64 or M/32. Sugar solutions of lower concentrations than M/64 caused no rise in the manometer. We will call this effect of the concentration of the solute on the initial rate of diffusion the gas pressure effect. Solutions of electrolytes show this gas pressure effect also, but it commences at somewhat higher concentrations than M/64, namely at M/16 or even M/8. Solutions of electrolytes of a lower concentration than M/16 or M/8 have a specific influence on the rate of diffusion of water through the membrane which is not found in the case of non-electrolytes.

When we separate a watery solution of an electrolyte of a concentration below M/16 from pure water by a collodion membrane, the water molecules diffuse through the membrane as if they were electrically charged—positively or negatively according to the nature of the ions present—and as if they were attracted electrostatically by ions of one sign and repelled by ions of the opposite sign. When we used solutions of electrolytes theoretically isosmotic with a M/64 cane sugar solution it was found that the influence of the nature of the electrolytes on the rate of diffusion of water through a collodion membrane could be expressed in the following two rules:

(1) Neutral solutions of salts possessing a univalent or a bivalent cation influence the rate of diffusion of water through a collodion membrane as if the water particles were charged positively and were attracted by the anion and repelled by the cation of the electrolytes; the attractive and repulsive action increasing with the number of charges of the ion and diminishing inversely with a quantity which we will designate arbitrarily as the 'radius' of the ion. The same rule applies to solutions of alkalies.

(2) Solutions of neutral or acid salts possessing a trivalent or tetravalent cation influence the rate of diffusion of water through a collodion membrane as if the particles of water were charged negatively and were attracted by the cation and repelled by the anion of the electrolyte. Solutions of acids and of neutral salts with monovalent or bivalent cation when rendered sufficiently acid obey the same rule.[5]

Thus the rate of diffusion of water into a neutral solution was considerably greater when the solution was M/128 NaCl than when it was M/64 cane sugar; and when different sodium or potassium salts were compared it was found that the rate increased with the valency of the anion of the salt in solution, sulfates and oxalates acting more powerfully than chlorides and nitrates, and citrates and ferrosulfocyanides more powerfully than sulfates and oxalates. The rate of diffusion of water was less when the solution was M/192 $CaCl_2$ than when it was M/64 cane sugar, and the same was true for all solutions of neutral salts with bivalent cation and monovalent anion. The attraction of M/128 solutions for water increased in the order $Li < Na < K$, showing the influence of the 'radius of the ion.' Solutions of alkalies like NaOH or KOH acted similarly to solutions of NaCl or KCl. All this was to be expected if water particles behaved as if they were positively charged, being attracted by the anion and repelled by the cation of the electrolyte.

In the case of electrolytes falling under rule 2, water particles behave as if they were negatively charged and attracted by the cation and repelled by the anion of the electrolyte with a force increasing with the number of charges of the ions. Thus solutions of Al_2Cl_6 attract water very powerfully, solutions of $Al_2(SO_4)_3$ of the same theoretical concentration act much more feebly and solutions of aluminium citrate have practically no more influence on the rate of diffusion of water than cane sugar solutions of the same concentration. When we render M/128 solutions of NaCl acid (by dissolving the salt in M/1024 HCl) the water particles diffusing through the membrane are negatively charged and are attracted by the Na ion of the solution. This is supported by the fact that M/192 $CaCl_2$ dissolved in M/1024 HCl (or HNO_3) attracts water much more powerfully than does M/128 NaCl of the same hydrogen ion concentration; and the attraction of M/512 Al_2Cl_6 of the same hydrogen ion concentration for water is still more powerful than that of $CaCl_2$. All this is intelligible on the assumption of an electrostatic influence of the ions upon negatively electrified particles of water—no matter what the nature or source of electrification of water may be. That water is indeed electrified in the sense expressed in the two rules was proved directly by experiments on electrical endosmose.

The collodion membranes are not only permeable to water but also to crystalloids in solutions. It could be shown by analytical experiments that the phenomena expressed in the two rules were not due to differences in the rate of diffusion of the solute. The reader will find a full description of these experiments in a recently published paper.[6]

3. The two rules mentioned before were based on experiments with solutions of about the same gas pressure, namely that of a M/64 sugar solution. When we compare the osmotic effect of different concentrations of sodium (or Li, K, NH_4) salts within the limit of M/8192 to about M/16 we find a curious phenomenon. In these experiments the solution of the electrolyte was put inside the collodion bag and the latter was dipped into a beaker with pure water. It was found that under these conditions the initial rise (i.e., the rise in the first ten or twenty minutes) of water in the collodion bag increased rapidly with the increase of the concentration of the solution, this initial rise reaching a maximum when the concentration of the electrolyte was about M/256. With a further increase of the concentration of the electrolyte the initial rate of diffusion of water from pure solvent into the solution dropped rapidly, reaching a minimum at about a concentration of M/16. We therefore notice the paradoxical fact that M/256 solutions of all these electrolytes attract water more powerfully than M/16 solutions of the same electrolytes. Thus in the case of a neutral solution of sodium oxalate the level of water rose in the manometer of the flask in twenty minutes to about 100 mm. when the concentration of the solution was M/1024, to 220 mm. when the concentration was M/256, but only to 100 mm. again when the concentration was M/16. While I do not wish to make any assumption concerning the source of the electrification of water and the mechanism by which

the electrolytes influence the rate of diffusion of water through a membrane it will simplify the presentation of my results if it is permitted to ascribe them to the attraction and repulsion of the charged particles of water by the ions. With this reservation we may say that the rise in the first part of the curve, in concentrations from 0 to about M/256, being caused by the prevalence of the attractive action of the anion upon the negatively charged particles of water, while the drop in the curve, when the concentration increases beyond M/256, is due to the fact that with a further increase in the concentration the repelling effect of the Na ion upon the water particles increases more rapidly than the attractive effect of the oxalate anion. With concentrations above M/16 or M/8 the gas pressure effect of the solution commences to prevail over the electrostatic effects of the ions and the rate of diffusion of water rises again with increasing concentration.

We may state incidentally that all these phenomena can be observed just as well in collodion membranes which have not been treated with gelatin, so that the gelatin plays no rôle in the action of the membrane on solutions of neutral or alkaline salts.

4. This influence of the concentration of electrolytes upon the rate of diffusion of water explains the phenomenon of negative osmosis. It had been known for more than fifty years through the experiments of Dutrochet and Graham which were recently confirmed by Flusin,[6] that solutions of certain acids, like tartaric and oxalic, when separated from pure water by a membrane of pig's bladder produce a negative osmosis, i.e., water diffuses from the solution to the pure solvent. This is, of course, exactly the reverse of what one should expect on the basis of van't Hoff's theory. The writer has investigated this phenomenon and he found that it holds with certain exceptions for all the acids and all the alkalies, *and that this expulsion of water from the solution (the so-called negative osmosis) occurs in exactly the same range of concentrations where the drop in the electrostatic attraction of sodium salts for water occurs, namely in concentrations from about M/256 to about M/8.* Collodion flasks were filled with distilled water and submersed in beakers filled with solutions of acids or alkalies of different concentrations. The volume of water in the flask instead of diminishing increased when the concentration of the acid was between M/256 and M/16 or M/8 and the increase was the more considerable the higher the concentration of the acid or alkali within the limits mentioned.

Our first rule states that in the presence of salts and alkalies with univalent and bivalent cation water diffuses through the collodion membrane as if its particles were positively charged. On the basis of this statement the initial expulsion of water by solutions of alkalies in concentrations above M/256 should be due to the fact that above a concentration of M/256 the repelling action of the cation upon the positively charged water particle increases more raipdly with increasing concentration of the elctrolyte than the attractive action of OH ions. When the cation is bivalent, e.g., when we use $Ca(OH)_2$ or $Ba(OH)_2$ as alkalies, the repelling action of the Ca and Ba ion with their two charges is so much stronger than the weak attractive action of the OH ions that water diffuses more rapidly from solution into pure water than pure water can diffuse into the solution, and the level of the water rises (during the first twenty minutes or more) in the pure solvent and falls in the solution. It harmonizes with our suggestion that the negative osmosis does not exist in the case of alkalies with monovalent cation like NaOH or KOH.

If the solution is an acid, water diffuses through the membrane as if its particles were negatively charged, being attracted by the H ion and repelled by the anion of the acid. In concentrations of acid of M/256 to about M/8 the solution expels during the first twenty minutes water into the pure solvent and the more the higher the concentration. This negative osmosis should be due to the fact that within this range the repelling action of the anion of the acid upon negatively charged water particles increases more rapidly with the concentration than the attractive action of hydrogen ion.

This suggestion is supported by the fact that the rate in which the acid solution expels water increases for the strong acids with the valency of the anion. Thus the amount of negative osmosis is small or negligible in the case of HCl or HNO_3, is considerable in the case of H_2SO_4 and oxalic acid, and still greater in the case of H_3PO_4. The phenomenon is not noticeable in the slightly dissociated acetic acid.

5. The definition of osmotic pressure as given in the introduction of this paper suggests that in the case of strictly semipermeable membranes the permanent osmotic pressure of the solution should show a simple relation to the difference in the initial rate of the diffusion of water in the two opposite directions through a membrane. Our experiments have shown that the initial rate of diffusion of water through a collodion membrane is determined for lower concentrations of electrolytes to a large extent by the electrostatic effects of the ions present and we should expect that these electrostatic effects would also influence the permanent osmotic pressure of solutions of electrolytes. Collodion membranes which are

permeable for solutions of crystalloids are impermeable for solutions of colloidal salts, e.g., the salts of gelatin. It can be shown that the permanent osmotic pressure of solutions of gelatin salts is influenced by the electrostatic action of ions in a similar way as is the rate of diffusion of water. I have found that water diffuses into neutral solutions of Na, K, Ca or Ba gelatinate as if the particles of water were positively charged. Since Ca and Ba (and all the other bivalent cations) have a greater repelling effect on positively charged particles of water than Li, Na, K or NH_4, the initial rate of diffusion of water should be greater when gelatin (in a 1% solution) is in combination with a monovalent cation than when it is in combination with a bivalent cation. I have tested this idea and found it confirmed. When we separate 1% gelatin solutions from distilled water by a collodion membrane the initial rate of diffusion of water into the solution is a little over twice as great when the gelatin exists in the form of sodium gelatinate than when it exists as calcium gelatinate, both having the same hydrogen ion concentration. The permanent osmotic pressures of the two types of solutions show also approximately the same ratio, being about or a little over twice as great in the case of sodium gelatinate as in the case of calcium gelatinate of the same concentration of gelatin as well as of hydrogen ions. Li, K, and NH_4 gelatinate behave like sodium gelatinate while Mg, Sr, and Ba gelatinate behave like calcium gelatinate.

Water particles behave like negatively charged particles in the presence of gelatin salts in which the gelatin is a cation, e.g., gelatin chloride or gelatin sulfate. If 1% solutions of these two gelatin salts of the same hydrogen ion concentration are prepared and put into collodion bags, water diffuses twice as rapidly into the gelatin chloride solution as into the gelatin sulfate solution. The osmotic pressures of the two solutions vary also as about 1:2 or a little less.[7]

The full report of the experiments on the influence of the concentration of electrolytes on the electrification and rate of diffusion of water through membranes will appear in the *Journal of General Physiology.*

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[2] Bartell, F. E., *J. Amer. Chem. Soc.*, 36, 1914, (646). Bartell, F. E., and Hocker, C. D., *Ibid.*, 38, 1916, (1029-1036).

[3] Bernstein, J., *Elektrobiologie*, 1912.

[4] Perrin, J., *J. Chem. Physique*, 2, 1904, (601); 3, 1905, (50).

[5] Loeb, J., *J. Gen. Physiol.*, 1, 1918-19, (717).

[6] Flusin, G., *Ann. chim. phys.*, 13, 1908, (480).

[7] Loeb, J., *J. Gen. Physiol.*, 2, 1919, No. 1.